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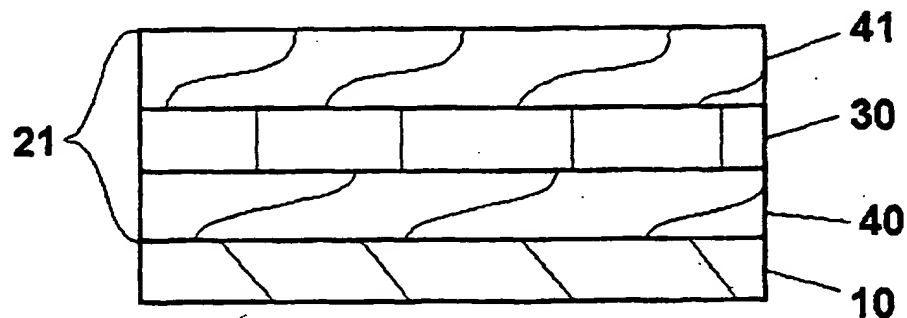
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(54) Title: **LITHIUM ANODES FOR ELECTROCHEMICAL CELLS**



(57) Abstract: Provided is an anode for use in electrochemical cells, wherein the anode active layer has a first layer comprising lithium metal and a multi-layer structure comprising single ion conducting layers and crosslinked polymer layers in contact with the first layer comprising lithium metal or in contact with an intermediate protective layer, such as a temporary protective metal layer, or plasma CO₂ treatment layers on the surface of the lithium-containing first layer. The anodes of the current invention are particularly useful in electrochemical cells comprising sulfur-containing cathode active materials, such as elemental sulfur.

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LITHIUM ANODES FOR ELECTROCHEMICAL CELLS

TECHNICAL FIELD

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The present invention relates generally to the field of lithium anodes for use in electrochemical cells. More particularly, the present invention pertains to an anode for use in an electrochemical cell comprising a first layer comprising lithium metal in contact with three or more overlying layers interposed between the lithium-containing layer and a non-aqueous electrolyte. The present invention also pertains to methods of forming such anodes, electrochemical cells comprising such anodes, and methods of making such cells.

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BACKGROUND

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Throughout this application, various publications, patents, and published patent applications are referred to by an identifying citation. The disclosures of the publications, patents, and published patent specifications referenced in this application are hereby incorporated by reference into the present disclosure to more fully describe the state of the art to which this invention pertains.

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There has been considerable interest in recent years in developing high energy density batteries with lithium containing anodes. Lithium metal is particularly attractive as the anode of electrochemical cells because of its extremely light weight and high energy density, compared for example to anodes, such as lithium intercalated carbon anodes, where the presence of non-electroactive materials increases weight and volume of the anode, and thereby reduces the energy density of the cells, and to other electrochemical systems with, for example, nickel or cadmium electrodes. Lithium metal anodes, or those comprising mainly lithium metal, provide an opportunity to construct cells which are lighter in weight, and which have a higher energy density than cells such as lithium-ion, nickel metal hydride or nickel-cadmium cells. These features are highly desirable for batteries for portable electronic devices such as cellular phones and laptop computers where a premium is paid for low weight. Unfortunately, the reactivity of lithium and the associated cycle life, dendrite formation, electrolyte compatibility, fabrication and safety problems have hindered the commercialization of lithium cells.

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The separation of a lithium anode from the electrolyte of the cell is desirable for reasons including the prevention of dendrites during recharging, reaction with the electrolyte, and cycle life. For example, reactions of lithium anodes with the electrolyte may result in the formation of resistive film barriers on the anode. This film barrier
5 increases the internal resistance of the battery and lowers the amount of current capable of being supplied by the battery at the rated voltage.

Many different solutions have been proposed for the protection of lithium anodes including coating the lithium anode with interfacial or protective layers formed from polymers, ceramics, or glasses, the important characteristic of such interfacial or protective
10 layers being to conduct lithium ions. For example, U.S. Pat. Nos. 5,460,905 and 5,462,566 to Skotheim describe a film of an n-doped conjugated polymer interposed between the alkali metal anode and the electrolyte. U.S. Pat. No. 5,648,187 to Skotheim and U.S. Pat. No. 5,961,672 to Skotheim *et al.* describe an electrically conducting crosslinked polymer film interposed between the lithium anode and the electrolyte, and methods of making the
15 same, where the crosslinked polymer film is capable of transmitting lithium ions. U.S. Pat. No. 5,314,765 to Bates describes a thin layer of a lithium ion conducting ceramic coating between the anode and the electrolyte. Yet further examples of interfacial films for lithium containing anodes are described, for example, in: U.S. Pat. Nos. 5,387,497 and 5,487,959 to Koksang; U.S. Pat. No. 4,917,975 to De Jonghe *et al.*; U.S. Pat. No. 5,434,021 to
20 Fauteux *et al.*; and U.S. Pat. No. 5,824,434 to Kawakami *et al.*

A single protective layer of an alkali ion conducting glassy or amorphous material for alkali metal anodes, for example, in lithium-sulfur cells, is described in U.S. Pat. No. 6,02,094 to Visco *et al.* to address the problem of short cycle life.

Despite the various approaches proposed for methods for forming lithium anodes
25 and the formation of interfacial or protective layers, there remains a need for improved methods, which will allow for increased ease of fabrication of cells, while providing for cells with long cycle life, high lithium cycling efficiency, and high energy density.

SUMMARY OF THE INVENTION

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The anode of the present invention for use in an electrochemical cell comprises: (i) a first anode active layer comprising lithium metal; and (ii) a multi-layer structure in contact with a surface layer of the first anode active layer; wherein the multi-layer

structure comprises three or more layers, wherein each of the three or more layers comprises a layer selected from the group consisting of single ion conducting layers and polymer layers. In one embodiment, the multi-layer structure comprises four or more layers.

5 In one embodiment of the present invention, an anode for use in an electrochemical cell, comprises an anode active layer, which anode active layer comprises: (i) a first layer comprising lithium metal; and (ii) a second layer of a temporary protective material in contact with a surface of the first layer. In one embodiment, the temporary protective material is a temporary protective metal that is capable of forming an alloy with lithium
10 metal or is capable of diffusing into lithium metal.

 In one embodiment, the temporary protective metal is selected from the group consisting of copper, magnesium, aluminum, silver, gold, lead, cadmium, bismuth, indium, gallium, germanium, zinc, tin, and platinum. In one embodiment, the temporary protective metal is copper.

15 In one embodiment, the thickness of the first layer is 2 to 100 microns.

 In one embodiment, the thickness of the second layer is 5 to 500 nanometers. In one embodiment, the thickness of the second layer is 20 to 200 nanometers.

 In one embodiment, the anode further comprises a substrate, wherein the substrate is in contact with a surface of the first layer on the side opposite the second layer. In one
20 embodiment, the substrate comprises a current collector. In one embodiment, the substrate is selected from the group consisting of metal foils, polymer films, metallized polymer films, electrically conductive polymer films, polymer films having an electrically conductive coating, electrically conductive polymer films having an electrically conductive metal coating, and polymer films having conductive particles dispersed therein.

25 In one embodiment, the anode further comprises a third layer, the third layer comprising a single ion conducting layer, wherein the third layer is in contact with the second layer on the side opposite to the first layer. In one embodiment, the single ion conducting layer of the third layer comprises a glass selected from the group consisting of lithium silicates, lithium borates, lithium aluminates, lithium phosphates, lithium
30 phosphorus oxynitrides, lithium silicosulfides, lithium germanosulfides, lithium lanthanum oxides, lithium tantalum oxides, lithium niobium oxides, lithium titanium oxides, lithium borosulfides, lithium aluminosulfides, and lithium phosphosulfides and combinations

thereof. In one embodiment, the single ion conducting layer of the third layer comprises a lithium phosphorus oxynitride.

In another embodiment, the anode further comprises a third layer, the third layer comprising a polymer, and wherein the third layer is in contact with the second layer on the side opposite to the first layer. In one embodiment, the polymer of the third layer is selected from the group consisting of electrically conductive polymers, ionically conductive polymers, sulfonated polymers, and hydrocarbon polymers. In one embodiment, the electrically conductive polymer is selected from the group consisting of poly(p-phenylene), polyacetylene, poly(phenylenevinylene), polyazulene, poly(perinaphthalene), polyacenes, and poly(naphthalene-2,6-diyl). In one embodiment, the polymer of the third layer is a crosslinked polymer.

In one embodiment, the anode further comprises a fourth layer, wherein the fourth layer is in contact with the third layer on the side opposite to the second layer. In one embodiment, the fourth layer comprises a polymer. In one embodiment, the polymer of the fourth layer is selected from the group consisting of electrically conductive polymers, ionically conductive polymers, sulfonated polymers, and hydrocarbon polymers. In one embodiment, the polymer of the fourth layer is a crosslinked polymer. In one embodiment, the fourth layer comprise a metal.

In one embodiment, the thickness of the third layer is in the range of 5 to 5000 nanometers. In one embodiment, the thickness of the fourth layer is in the range of 5 to 5000 nanometers.

Another aspect of the present invention pertains to methods of preparing an anode for use in an electrochemical cell, wherein the anode comprising an anode active layer, as described herein, is formed by the steps of:

- (a) depositing onto a substrate, as described herein, a first layer comprising lithium metal, as described herein; and
- (b) depositing over the first layer a second layer of a temporary protective metal, as described herein;

wherein the temporary protective metal is capable of forming an alloy with lithium metal or is capable of diffusing into lithium metal.

In one embodiment, the temporary protective metal is selected from the group consisting of copper, magnesium, aluminum, silver, gold, lead, cadmium, bismuth, indium, gallium, germanium, zinc, tin, and platinum.

In one embodiment, the first layer is deposited in step (a) by a method selected from the group consisting of thermal evaporation, sputtering, jet vapor deposition, laser ablation, and extrusion.

5 In one embodiment, the second layer is deposited in step (b) by a method selected from the group consisting of thermal evaporation, sputtering, jet vapor deposition, laser ablation, and extrusion.

In one embodiment, the method comprises after step (b), a step (c) of depositing a third layer comprising a single ion conducting layer, as described herein, over the second layer. In one embodiment, the third layer is deposited by a method selected from the
10 group consisting of sputtering, thermal evaporation, laser ablation, chemical vapor deposition, and jet vapor deposition.

In another embodiment, the method comprises after step (b), a step (c) of depositing a third layer comprising a polymer, as described herein, over the second layer. In one embodiment, the third layer is deposited by a method selected from the group
15 consisting of thermal evaporation, sputtering, laser ablation, chemical vapor deposition, and jet vapor deposition. In one embodiment, the polymer of the third layer is deposited by the method of flash evaporation.

In another embodiment, the method of the present invention comprises, after step (c), a step (d) of depositing a fourth layer, wherein said fourth layer comprises a polymer.

20 Another aspect of the present invention pertains to an electrochemical cell comprising: (a) a cathode comprising an electroactive sulfur-containing material; (b) an anode; and (c) a non-aqueous electrolyte interposed between the anode and the cathode, wherein the anode comprises: (i) a first anode active layer comprising lithium metal; and
25 (ii) a multi-layer structure in contact with a surface layer of the anode active layer, wherein the multi-layer structure comprises three or more layers, wherein each of the three or more layers comprises a layer selected from the group consisting of single ion conducting layers and polymer layers.

In one embodiment, the thickness of the first anode active layer is from 2 to 100 microns.

30 In one embodiment, the thickness of the multi-layer structure is 0.5 to 10 microns. In one embodiment, the thickness of the multi-layer structure is 1 to 5 microns.

In one embodiment, the multi-layer structure comprises four or more layers.

In one embodiment, the multi-layer structure further comprises a metal alloy layer, wherein the metal alloy comprises a metal selected from the group consisting of Zn, Mg, Sn, and Al.

5 In one embodiment, the polymer layer of the multi-layer structure comprises a polymer layer formed from the polymerization of one or more acrylate monomers selected from the group consisting of alkyl acrylates, glycol acrylates, and polyglycol acrylates. In one embodiment, the single ion conducting layer of the multi-layer structure comprises a glass selected from the group consisting of lithium silicates, lithium borates, lithium aluminates, lithium phosphates, lithium phosphorus oxynitrides, lithium silicosulfides,
10 lithium germanosulfides, lithium lanthanum oxides, lithium tantalum oxides, lithium niobium oxides, lithium titanium oxides, lithium borosulfides, lithium aluminosulfides, and lithium phosphosulfides and combinations thereof. In one embodiment, the single ion conducting layer comprises a lithium phosphorus oxynitride.

In one embodiment, the non-aqueous electrolyte is a liquid.

15 In one embodiment, the first anode active layer further comprises an intermediate layer of a temporary protective metal layer or a plasma CO₂ treatment layer, which intermediate layer is interposed between the first anode active layer and the multi-layered structure.

In one embodiment, the electroactive sulfur-containing material of the cathode
20 comprises elemental sulfur. In one embodiment, the electroactive sulfur-containing material comprises an electroactive sulfur-containing organic polymer, wherein the sulfur-containing organic polymer, in its oxidized state, comprises one or more polysulfide moieties, $-S_m^-$, where m is an integer equal to or greater than 3. In one embodiment, the cathode active material comprises an electroactive sulfur-containing organic polymer,
25 wherein the sulfur-containing organic polymer, in its oxidized state, comprises one or more polysulfide moieties, $-S_m^-$, where m is an integer equal to or greater than 3. In one embodiment, the cathode active material comprises an electroactive sulfur-containing organic polymer, wherein the sulfur-containing organic polymer, in its oxidized state, comprises one or more polysulfide moieties, S_m^{2-} , where m is an integer equal to or greater
30 than 3.

A further aspect of the present invention pertains to an electrochemical cell comprising:

(a) a cathode comprising a cathode active material;

(b) an anode; and

(c) a non-aqueous electrolyte interposed between the anode and the cathode;

wherein the anode comprises an anode active layer, which anode active layer comprises:

- 5 (i) a first layer comprising lithium metal, as described herein; and
 (ii) a second layer of a temporary protective metal, as described herein, in contact with a surface of the first layer;

wherein the temporary protective metal is capable of forming an alloy with lithium or is capable of diffusing into lithium metal.

10 In one embodiment, the temporary protective metal is characterized by forming an alloy with, dissolving into, blending with, or diffusing into the lithium metal of the first layer during electrochemical cycling of the cell.

 In one embodiment, the temporary protective metal is characterized by forming an alloy with, dissolving in, blending with, or diffusing into the lithium metal of the first layer
15 prior to electrochemical cycling of the cell.

 In one embodiment of the cell of the present invention, the anode further comprises a substrate, as described herein.

 In one embodiment of the cell of the present invention, the anode further comprises a third layer comprising a single ion conducting layer, as described herein. In one
20 embodiment, the anode further comprises a third layer comprising a polymer, as described herein.

 In one embodiment of the cell of the present invention, the electrolyte is selected from the group consisting of liquid electrolytes, solid polymer electrolytes, and gel polymer electrolytes. In one embodiment, the electrolyte comprises a separator selected
25 from the group consisting of polyolefin separators and microporous xerogel layer separators.

 In one embodiment of the cell of the present invention, the cathode active material comprises one or more materials selected from the group consisting of electroactive metal chalcogenides, electroactive conductive polymers, and electroactive sulfur-containing
30 materials, and combinations thereof.

 In one embodiment, the cathode active material comprises electroactive sulfur-containing materials, as described herein.

In one embodiment, the cell is a secondary cell. In one embodiment, the cell is a primary cell.

Another aspect of the present invention pertains to a method for making an electrochemical cell, as described herein, the method comprising the steps of:

- 5 (a) providing a cathode comprising a cathode active material, as described herein;
(b) providing an anode, wherein the anode comprises an anode active layer, which anode active layer comprises:

(i) a first layer comprising lithium metal, as described herein; and

- 10 (ii) a second layer of a temporary protective metal, as described herein, in contact with a surface of the first layer; and

(c) providing a non-aqueous electrolyte, as described herein, wherein the electrolyte is interposed between the anode and the cathode;

wherein the temporary protective metal is capable of forming an alloy with lithium metal or is capable of diffusing into lithium metal.

- 15 In one embodiment of the methods of making an electrochemical cell, the temporary protective metal is characterized by forming an alloy with, dissolving in, blending with, or diffusing into the lithium metal of the first layer during electrochemical cycling of the cell.

20 In one embodiment of the methods of making an electrochemical cell, the temporary protective metal is characterized by forming an alloy with, dissolving in, blending with, or diffusing into the lithium metal of the first layer prior to electrochemical cycling of the cell.

25 In one embodiment of the methods of making an electrochemical cell, the anode further comprises a third layer, the third layer comprising a material selected from the group consisting of single ion conducting materials, as described herein, and polymers, as described herein, wherein the third layer is in contact with the temporary protective metal layer on the side opposite to the first layer comprising lithium.

In one embodiment of the methods of making an electrochemical cell, the anode comprises a fourth layer, as described herein.

- 30 As will be appreciated by one of skill in the art, features of one aspect or embodiment of the invention are also applicable to other aspects or embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a sectional view of one embodiment of the anode of the present invention comprising (a) a first layer 10 comprising lithium metal, and (b) a multi-layer structure 21 comprising a single ion conducting layer 40, a polymer layer 30, and a single ion conducting layer 41.

Figure 2 shows a sectional view of one embodiment of the anode of the present invention comprising (a) a first layer 10 comprising lithium metal, and (b) a multi-layer structure 20 comprising a polymer layer 30, a single ion conducting layer 40, and a polymer layer 31.

Figure 3 shows a sectional view of one embodiment of the anode of the present invention comprising (a) a first layer 10 comprising lithium metal, and (b) a multi-layer structure 22 comprising a polymer layer 30, a single ion conducting layer 40, metal layer 50, and a polymer layer 31.

Figure 4 shows a sectional view of one embodiment of the anode of the present invention comprising (a) a first layer 10 comprising lithium metal, and (b) a multi-layer structure 23 comprising a polymer layer 30, a single ion conducting layer 40, a polymer layer 31, a single ion conducting layer 41, and a polymer layer 32.

Figure 5 shows a sectional view of one embodiment of the anode of the present invention comprising (a) a first layer 10 comprising lithium metal, and (b) a multi-layer structure 24 comprising a surface layer 50, a single ion conducting layer 40, a polymer layer 30, a single ion conducting layer 41, and a polymer layer 31.

DETAILED DESCRIPTION OF THE INVENTION

The difficulties encountered by the reactivity of a lithium anode surface of, for example, a Li/S electrochemical cell during storage or cycling, may, according to the present invention, be solved by the use of an anode comprising a multi-layer structure. The multi-layer structure of the anode allows passage of lithium ions while acting as a barrier to other cell components more effectively, than single or dual layer interfacial films.

One aspect of the present invention pertains to an anode for use in an electrochemical cell, wherein the anode comprises:

- (i) a first anode active layer comprising lithium metal; and
- (ii) a multi-layer structure in contact with a surface of the first layer; wherein the multi-layer structure comprises three or more layers, wherein each of the layers comprises a single ion conducting layer or a polymer layer.

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Anode Active Layers

The first layer of the anode of the present invention comprises lithium metal as the anode active material. In one embodiment of the anodes of the present invention, the first anode active layer of the anode is lithium metal. The lithium metal may be in the form of a lithium metal foil or a thin lithium film that has been deposited on a substrate, as described below. If desirable for the electrochemical properties of the cell, the lithium metal may be in the form of a lithium alloy such as, for example, a lithium-tin alloy or a lithium aluminum alloy.

The thickness of the first layer comprising lithium may vary from about 2 to 200 microns. The choice of the thickness will depend on cell design parameters such as the excess amount of lithium desired, cycle life, and the thickness of the cathode electrode. In one embodiment, the thickness of the first anode active layer is in the range of about 2 to 100 microns. In one embodiment, the thickness of the first anode active layer is in the range of about 5 to 50 microns. In one embodiment, the thickness of the first anode active layer is in the range of about 5 to 25 microns. In another embodiment, the thickness of the first anode active layer is in the range of about 10 to 25 microns.

The anodes of the present invention may further comprise a substrate, as is known in the art, on the surface of the first anode active layer on the side opposite to that of the multi-layer structure. Substrates are useful as a support on which to deposit the first layer comprising the anode active material, and may provide additional stability for handling of thin lithium film anodes during cell fabrication. Further, in the case of conductive substrates, these may also function as a current collector useful in efficiently collecting the electrical current generated throughout the anode and in providing an efficient surface for attachment of the electrical contacts leading to the external circuit. A wide range of substrates are known in the art of anodes. Suitable substrates include, but are not limited to, those selected from the group consisting of metal foils, polymer films, metallized polymer films, electrically conductive polymer films, polymer films having an electrically conductive coating, electrically conductive polymer films having an electrically conductive

metal coating, and polymer films having conductive particles dispersed therein. In one embodiment, the substrate is a metallized polymer film.

In one aspect of the anode of the present invention, the multi-layered structure may be placed in direct contact with a surface of the first anode active layer comprising lithium.

5 In another embodiment of the present invention, it may be desirable for the anode active layer to further comprise an intermediate layer interposed between a surface of the first anode active layer and a surface of the multi-layered structure. Such intermediate layers may, for example, comprise a temporary protective metal layer, or a layer formed from the reaction of CO₂, SO₂, or other reactive gaseous material with the lithium surface to provide
10 either a temporary protective material layer or a permanent interfacial protective layer.

The difficulties encountered by the reactivity of a lithium surface during deposition of, for example, anode stabilizing layers, may, according to the present invention, be solved by depositing over the lithium surface prior to coating or depositing such a stabilizing or other layer, a layer of a temporary protective material, such as, for example,
15 a temporary protective metal. The temporary protective material layer acts as a barrier layer to protect the lithium surface during deposition of other anode layers, such as during the deposition of the multi-layer structure of the present invention. Suitable temporary protective material layers include, but are not limited to, temporary metal layers. Further, the temporary protective layer may allow transportation of the lithium films from one
20 processing station to the next without undesirable reactions occurring at the lithium surface during assembly of cells, or for solvent coating of layers onto the anode.

In one embodiment of the anode of the present invention, a layer of a temporary protective material may be placed in contact with the first anode active layer comprising lithium metal on the side of the anode active layer facing the multi-layer structure. In one
25 embodiment, the temporary protective material is a temporary metal layer. The temporary protective metal is selected for its ability to form an alloy with, dissolve into, blend with, or diffuse into the lithium metal of the first layer comprising lithium metal. In one embodiment, the metal of the temporary protective layer is selected from the group consisting of copper, magnesium, aluminum, silver, gold, lead, cadmium, bismuth, indium, gallium, germanium, zinc, tin, and platinum. In a preferred embodiment the metal of the
30 temporary protective metal layer is copper.

The thickness of the temporary protective metal layer interposed between the first anode active layer and the multi-layer structure is selected to provide the necessary

protection to the layer comprising lithium, for example, during subsequent treatments to deposit other anode or cell layers, such as interfacial or protective layers. It is desirable to keep the layer thickness as thin as possible while providing the desired degree of protection so as to not add excess amounts of non-active materials to the cell which would increase the weight of the cell and reduce its energy density. In one embodiment of the present invention, the thickness of the temporary protective layer is about 5 to 500 nanometers. In one embodiment of the present invention, the thickness of the temporary protective layer is about 20 to 200 nanometers. In one embodiment of the present invention, the thickness of the temporary protective layer is about 50 to 200 nanometers. In one embodiment of the present invention, the thickness of the temporary protective layer is about 100 to 150 nanometers.

During subsequent storage of an anode of this invention, comprising the first anode active layer and the temporary protective metal layer, or during storage of an electrochemical cell into which an anode of this invention is assembled, or during electrochemical cycling of the cell comprising an anode of the present invention, the temporary protective metal layer is capable of forming an alloy with, dissolving into, blending with, or diffusing into the lithium metal to yield a single anode active layer comprising lithium metal. Lithium metal is known to alloy with certain metals as described herein, and has further been observed to diffuse or alloy with thin layers of certain other metals such as, for example, copper. The interdiffusion or alloying can be assisted by heating the anode assembly. Further it has been found that alloying or diffusion of the temporary protective metal layer and lithium can be slowed or prevented by storage of the anode at low temperatures, such as at or below 0 °C. This feature may be utilized in the method of preparing anodes of the present invention.

The anode active layers of the present invention, further comprising a temporary metal layer or other layer, such as CO₂ or SO₂ induced layers, are especially desirable when an interfacial layer of some type is desired between the lithium surface and the electrolyte. For example, when a single ion conducting layer is desired at the lithium interface, it is preferable to deposit this directly on the lithium surface. However, the precursors to or components of such an interfacial layer may react with lithium to produce undesirable by-products or result in undesirable changes in the morphology of the layers. By depositing a temporary protective metal layer or other intermediate layer on the lithium surface prior to depositing the interfacial layer such as the multi-layer structure of the

present invention, side reactions at the lithium surface may be eliminated or significantly reduced. For example, when an interfacial film of a lithium phosphorus oxynitride, as described in U.S. Patent No. 5,314,765 to Bates, is deposited in a nitrogen atmosphere by sputtering of Li_3PO_4 onto a lithium surface, the nitrogen gas may react with lithium to
5 form lithium nitride (LiN_3) at the anode surface. By depositing a layer of a temporary protective metal, for example, copper over the lithium surface, the interfacial layer may be formed without the formation of lithium nitride.

Multi-Layered Structure

10 The anodes of the present invention comprise one or more single ion conducting layers or one or more polymer layers in contact in a multi-layer structure with a surface of a first anode active layer, as described herein. Such combinations that result in a total of three or more layers are referred to herein as "multi-layered structures". In the case of an intermediate layer, such as a temporary protective material layer on the first anode active
15 layer the multi-layer structure is not in contact to the first anode active layer comprising lithium metal and therefore is in contact to the intermediate layer.

In one embodiment of the present invention, where such an intermediate layer is present, the anode comprises a third layer, which third layer is in contact with a second or intermediate layer, on the side opposite to the first anode active layer, where the first anode
20 active layer comprises lithium metal and where the second or intermediate layer is a temporary protective metal layer. This third layer may function as an interfacial layer, for example, as an anode stabilizing or as an anode protective layer between the anode active layer and the electrolyte of the cell. In one embodiment, the third layer is a single ion conducting layer. In one embodiment, the third layer comprises a polymer. Other types of
25 interfacial or protective layers may also be deposited as a third layer, as are known in the art.

The thickness of the third layer of the anode of the present invention may vary over a wide range from about 5 nanometers to about 5000 nanometers, and is dependent on the thickness of the layer required to provide the desired beneficial effect of the layer while
30 maintaining properties needed for cell construction such as flexibility and low interfacial resistance. In one embodiment, the thickness of the third layer is in the range of about 10 nanometers to 2000 nanometers. In one embodiment, the thickness is in the range of about

50 nanometers to 1000 nanometers. In one embodiment, the thickness is in the range of about 100 nanometers to 500 nanometers.

The anode of the present invention may further comprise a fourth layer in contact with a surface of the third layer. A fourth layer may be desirable when the components of the third layer, which functions to stabilize or protect the anode active layer comprising lithium, may be unstable to components present in the electrolyte. This fourth layer should be conductive to lithium ions, preferably nonporous to prevent penetration by electrolyte solvents, compatible with electrolyte and the third layer, and flexible enough to accommodate for volume changes in the layers occurring during discharge and charge.

The fourth layer should further be insoluble in the electrolyte. As the fourth layer is not directly in contact with the lithium layer, compatibility with metallic lithium is not necessary. Examples of suitable fourth layers include, but are not limited to, organic or inorganic solid polymer electrolytes, electrically and ionically conducting polymers, and metals with certain lithium solubility properties. In one embodiment, the fourth layer comprises a polymer layer, wherein the fourth layer is in contact with the third layer on the side opposite to said second layer. In one embodiment, the polymer of the fourth layer is selected from the group consisting of electrically conductive polymers, ionically conductive polymers, sulfonated polymers, and hydrocarbon polymers. Further examples of suitable polymers for use in the fourth layer of the present invention are those described in U.S. Patent Application Serial No. 09/399,967 to Ying *et al.* of the common assignee for protective coating layers.

In a preferred embodiment of the present invention, the anode comprises a multi-layered structure in contact with a surface of the first anode active layer comprising lithium metal, wherein the multi-layered structure comprises three or more layers, and wherein the multi-layered structure comprises one or more single ion conducting layers and one or more polymer layers. Various embodiments of the present invention are illustrated in Figures 1-5, which are not drawn to scale. In one embodiment, the multi-layered structure comprises alternating single ion conducting layers and polymer layers, as illustrated in Figures 1, 2, and 4.

For example, a three layer multi-layer structure may comprise a first single ion conducting layer 40 in contact with a surface of the first anode active layer comprising lithium metal 10, a polymer layer 30 in contact with a surface of the first single ion

conducting layer 40, and a second single ion conducting layer 41 in contact with the surface of the polymer layer 30, as illustrated in Figure 1.

More preferably, for example, a three layer multi-layer structure may comprise a first polymer layer 30 in contact with a surface of the first anode active layer comprising lithium metal 10, a single ion conducting layer 40 in contact with the first polymer layer 30, and a second polymer layer 31 in contact with the single ion conducting layer 40, as illustrated in Figure 2.

In one embodiment, the multi-layer structure comprises three or more layers, wherein the multi-layered structure comprises one or more single ion conducting layers and one or more polymer layers. In another embodiment, the multi-layer structures comprise four or more layers, wherein the multi-layered structure comprises one or more single ion conducting layers and one or more polymer layers. In yet another embodiment, the multilayered structure comprises five or more layers, as illustrated in Figure 4.

The thickness of the multi-layer structure of the present invention may vary over a range from about 0.5 microns to about 10 microns. In a preferred embodiment, the thickness of the multi-layer structure may range from about 1 micron to about 5 microns.

Suitable single ion conducting layers for use in the anodes of the present invention include, but are not limited to, inorganic, organic, and mixed organic-inorganic polymeric materials. The term "single ion conducting layer," as used herein, pertains to a layer which selectively or exclusively allows passage of singly charged cations. Single ion conducting layers have the capability of selectively or exclusively transporting cations, such as lithium ions, and may comprise polymers such as, for example, disclosed in U.S. Pat. No. 5,731,104 to Ventura, *et al.* In one embodiment, the single ion conducting layer comprises a single ion conducting glass conductive to lithium ions. Among the suitable glasses are those that may be characterized as containing a "modifier" portion and a "network" portion, as known in the art. The modifier is typically a metal oxide of the metal ion conductive in the glass. The network former is typically a metal chalcogenide, such as for example, a metal oxide or sulfide.

Preferred single ion conducting layers for use in the anodes of the present invention include, but are not limited to, glassy layers comprising a glassy material selected from the group consisting of lithium silicates, lithium borates, lithium aluminates, lithium phosphates, lithium phosphorus oxynitrides, lithium silicosulfides, lithium germanosulfides, lithium lanthanum oxides, lithium titanium oxides, lithium borosulfides,

lithium aluminosulfides, and lithium phosphosulfides, and combinations thereof. In one embodiment, the single ion conducting layer comprises a lithium phosphorus oxynitride. Electrolyte films of lithium phosphorus oxynitride are disclosed, for example, in U.S. Pat. No. 5,569,520 to Bates. A thin film layer of lithium phosphorus oxynitride interposed
5 between a lithium anode and an electrolyte is disclosed, for example, in U.S. Pat. No. 5,314,765 to Bates. The selection of the single ion conducting layer will be dependent on a number of factors including, but not limited to, the properties of electrolyte and cathode used in the cell.

Suitable polymer layers for use in the anodes of the present invention, include, but
10 are not limited to, those selected from the group consisting of electrically conductive polymers, ionically conductive polymers, sulfonated polymers, and hydrocarbon polymers. The selection of the polymer will be dependent on a number of factors including, but not limited to, the properties of electrolyte and cathode used in the cell. Suitable electrically conductive polymers include, but are not limited to, those described in U.S. Pat. No.
15 5,648,187 to Skotheim, for example, including, but not limited to, poly(p-phenylene), polyacetylene, poly(phenylenevinylene), polyazulene, poly(perinaphthalene), polyacenes, and poly(naphthalene-2,6-diyl). Suitable ionically conductive polymers include, but are not limited to, ionically conductive polymers known to be useful in solid polymer electrolytes and gel polymer electrolytes for lithium electrochemical cells, such as, for
20 example, polyethylene oxides. Suitable sulfonated polymers include, but are not limited to, sulfonated siloxane polymers, sulfonated polystyrene-ethylene-butylene polymers, and sulfonated polystyrene polymers. Suitable hydrocarbon polymers include, but are not limited to, ethylene-propylene polymers, polystyrene polymers, and the like.

Also preferred for the polymer layers of the multi-layered structure of the present
25 invention, are crosslinked polymer materials formed from the polymerization of monomers including, but are not limited to, alkyl acrylates, glycol acrylates, polyglycol acrylates, polyglycol vinyl ethers, polyglycol divinyl ethers, and those described in U.S. Patent Application Serial No. 09/399,967 to Ying *et al.* of the common assignee for protective coating layers for separator layers. For example, one such crosslinked polymer material is
30 polydivinyl poly(ethylene glycol). The crosslinked polymer materials may further comprise salts, for example, lithium salts, to enhance ionic conductivity. In one embodiment, the polymer layer of the multi-layered structure comprises a crosslinked polymer.

The outer layer of the multi-layered structure, i.e. the layer that is in contact with the electrolyte or separator layer of the cell, should be selected for properties such as protection of underlying layers which may be unstable to components present in the electrolyte. This outer layer should be conductive to lithium ions, preferably nonporous to prevent penetration by electrolyte solvents, compatible with electrolyte and the underlying layers, and flexible enough to accommodate for volume changes in the layers observed during discharge and charge. The outer layer should further be stable and preferably insoluble in the electrolyte.

Examples of suitable outer layers include, but are not limited to, organic or inorganic solid polymer electrolytes, electrically and ionically conducting polymers, and metals with certain lithium solubility properties. In one embodiment, the polymer of the outer layer is selected from the group consisting of electrically conductive polymers, ionically conductive polymers, sulfonated polymers, and hydrocarbon polymers. Further examples of suitable polymers for use in the outer layer of the present invention are those described in U.S. Patent Application Serial No. 09/399,967 to Ying *et al.* of the common assignee for protective coating layers of coated separators.

In one embodiment of the present invention, the multi-layer structure may further comprise a metal alloy layer. The term "metal alloy layer," as used herein, pertains to lithiated metal alloy layers. The lithium content of the metal alloy layer may vary from about 0.5 % by weight to about 20 % by weight, depending, for example, on the specific choice of metal, the desired lithium ion conductivity, and the desired flexibility of the metal alloy layer. Suitable metals for use in the metal alloy layer include, but are not limited to, Al, Zn, Mg, Ag, Pb, Cd, Bi, Ga, In, Ge, and Sn. Preferred metals are, Zn, Mg, Sn, and Al. The thickness of the metal alloy layer may vary over a range from about 10 nm to about 1000 nm (1 micron). The metal alloy layer may be placed between polymer layers, between ion conducting layers, or between an ion conducting layer and a polymer layer, as illustrated in Figure 3. In one embodiment, the metal alloy layer is the outer layer of the multi-layered structure.

The anode of the present invention may have the multi-layer structure comprising three or more layers in contact with a surface of the first anode active layer comprising lithium metal, in contact with a surface of a second or intermediate temporary protective metal layer, or in contact with a surface layer formed on the first anode active layer, such as, for example, from reaction with CO₂ or SO₂. In one embodiment of the present

invention, the multi-layer structure is formed on a surface of the first anode active layer comprising lithium metal. In one embodiment of the present invention, a layer from the reaction of the first anode active layer comprising lithium metal with CO₂ or SO₂ is interposed between the multi-layer structure and the first anode active layer comprising lithium metal, wherein the multi-layer structure is formed on a surface of the reacted layer, as illustrated in Figure 5.

Multi-layer structures of the present invention possess properties superior to those of the individual layers which comprise the multi-layer. Each of the layers of the multi-layer structure, for example, the single ion conducting layers, the polymer layers, and the metal alloy layers, possess desirable properties but at the same time possess certain undesirable properties. For example, single ion conducting layers, especially vacuum deposited single ion conducting layers, are flexible as thin films but as they become thicker grow defects, such as pinholes and rougher surfaces. Metal alloy layers, for example, may block liquid and polysulfide migration, and are very ductile and flexible in thin film form but may interdiffuse with lithium and are electron conducting. Polymer layers and especially crosslinked polymer layers, for example, can provide very smooth surfaces, add strength and flexibility, and may be electron insulating. In the multi-layer structures of the present invention comprising three or more layers comprising one or more single ion conducting layers and one or more polymer layers, and optionally one or more metal alloy layers, it is possible to obtain essentially defect free structures. For example, a crosslinked polymer layer deposited over a single ion conducting layer may smooth the surface and thereby minimize defects in subsequent single ion conducting layers deposited upon it. The crosslinked polymer layer may be viewed as decoupling defects in layers on either side of it. Although the multi-layer structures consisting of three layers are effective in defect reduction of the anode interfacial layer, additional benefit may be gained from four or more layers. The benefits of a defect free layer or structure include efficient exclusion of undesirable species from the lithium surface, which can lead to dendrite formation, self discharge, and loss of cycle life. Other benefits of the multi-layer structure include an increased tolerance of the volumetric changes which accompany the migration of lithium back and forth from the anode during the cycles of discharge and charge of the cell, and improved robustness to withstand stresses during manufacturing processes.

The anodes of the present invention may be assembled into cells by combining with an electrolyte and a cathode comprising a cathode active material, as described

herein. The anodes may also be formed with other alkali or alkaline earth metal anode active materials by suitable choice of the multi-layered structure, and if desired by the presence of a temporary protective metal layer or other intermediate layer between the anode active layer and the multi-layered structure.

5

Methods of Making Anodes

Another aspect of the present invention pertains to a method of preparing an anode for use in an electrochemical cell, wherein the anode comprises:

- (i) a first anode active layer comprising lithium metal; and
- 10 (ii) a multi-layer structure in contact with a surface layer of the first anode active layer; wherein the multi-layer structure comprises three or more layers, wherein each of said layers comprises a single ion conducting layer or a cross-linked polymer layer, and is formed by the steps of:
 - (a) depositing onto a substrate a first anode active layer comprising lithium metal,
 - 15 or alternatively, providing a lithium metal foil as a first anode active layer;
 - (b) depositing over the first anode active layer a polymerizable monomer layer;
 - (c) polymerizing the monomer layer of step (b) to form a first polymer layer;
 - (d) depositing over the polymer layer of step (c) a first single ion conducting layer;
 - (e) depositing over the first single ion conducting layer of step (d) a second
 - 20 polymerizable monomer layer; and
 - (f) polymerizing the monomer layer of step (e) to form a second polymer layer to form a multi-layer structure comprising a single ion conducting layer and two polymer layers.

The method of the present invention may further comprise, subsequent to step (a) and prior to step (b), the step of treating the first anode active layer comprising lithium metal with CO₂ or SO₂, or depositing a layer of a temporary protective material, such as a temporary protective metal, as described herein.

The method of the present invention may further comprise, subsequent to step (f), repeating the steps (d), (e) and (f) one or more times to form a multi-layer structure comprising four or more layers.

30

Similarly, multi-layered structures may be formed by depositing over a first anode active layer a first layer of a single ion conducting layer, followed by a first polymer layer,

and subsequently a second ion conducting layer. If a metal alloy layer is desired in the structure, this may be deposited after any one of steps (c), (d), or (f).

In the method of the present invention, the polymerizable monomer layer of steps (b) and (e) may comprise dissolved lithium salts.

5 In one embodiment of the present invention, a method of preparing an anode for use in an electrochemical cell, wherein the anode comprises:

(i) a first anode active layer comprising lithium metal; and

(ii) a multi-layer structure in contact with a surface layer of the first anode active layer; wherein the multi-layer structure comprises three or more layers, wherein each of
10 said layers comprises a single ion conducting layer or a cross-linked polymer layer, and is formed by the steps of:

(a) depositing onto a substrate a first anode active layer comprising lithium metal, or alternatively, providing a lithium metal foil as a first anode active layer;

(b) depositing over the first anode active layer a first polymer layer;

15 (c) depositing over the polymer layer of step (b) a first single ion conducting layer; and

(d) depositing over the first single ion conducting layer of step (c) a second polymer layer to form a multi-layer structure comprising a single ion conducting layer and two cross-linked polymer layers.

20 In the method of the present invention, the polymer layer of steps (b) and (d) may comprise dissolved lithium salts.

Another aspect of the present invention pertains to a method of preparing an anode active layer comprising a temporary protective metal layer for use in an electrochemical cell, wherein the anode active layer is formed by the steps of:

25 (a) depositing onto a substrate a first anode active layer comprising lithium metal, or alternatively, providing a lithium metal foil as a first anode active layer; and

(b) depositing over the first anode active layer a second layer of a temporary protective metal, wherein the temporary protective metal is selected from the group consisting of copper, magnesium, aluminum, silver, gold, lead, cadmium, bismuth, indium, gallium, germanium, zinc, tin, and platinum; and wherein the temporary protective metal is
30 capable of forming an alloy with lithium metal or diffusing into lithium metal.

The method of forming an anode active layer comprising a temporary protective layer of the present invention, may further comprise after step (b), a step (c) of depositing

a third layer over the second layer formed in step (b), wherein the third layer comprises a single ion conducting layer, as described herein, or a polymer, as described herein. The method may further comprise after step (c), a step (d) of depositing a fourth layer over the third layer, wherein the fourth layer comprises a polymer.

5 The layers of the anode of the present invention may be deposited by any of the methods known in the art, such as physical or chemical vapor deposition methods, extrusion, and electroplating. Examples of suitable physical or chemical vapor deposition methods include, but are not limited to, thermal evaporation (including, but not limited to, resistive, inductive, radiation, and electron beam heating), sputtering (including, but not
10 limited to, diode, DC magnetron, RF, RF magnetron, pulsed, dual magnetron, AC, MF, and reactive), chemical vapor deposition, plasma enhanced chemical vapor deposition, laser enhanced chemical vapor deposition, ion plating, cathodic arc, jet vapor deposition, and laser ablation.

 Preferably the deposition of the layers is carried out in a vacuum or inert
15 atmosphere to minimize side reactions in the deposited layers which would introduce impurities into the layers or which may affect the desired morphology of the layers. It is preferable that anode active layer and the layers of the multi-layered structure are deposited in a continuous fashion in a multistage deposition apparatus. If the anode active layer comprises a temporary protective metal layer, this layer is capable of providing
20 protection for the anode active layer if the layers of the multi-layered structure are deposited in a different apparatus.

 Preferred methods for the deposition of the first anode active layer comprising lithium metal on to a substrate are those selected from the group consisting of thermal evaporation, sputtering, jet vapor deposition, and laser ablation. In one embodiment, the
25 first layer is deposited by thermal evaporation. Alternatively, the first anode active layer may comprise a lithium foil, or a lithium foil and a substrate, which may be laminated together by a lamination process as known in the art, to form the first layer.

 Suitable methods for depositing the temporary protective metal layer include, but are not limited to, thermal evaporation, sputtering, jet vapor deposition, and laser ablation.
30 In one embodiment, the temporary protective metal layer is deposited by thermal evaporation or sputtering.

The layers of the multi-layered structure comprising a single ion conducting layer or a polymer layer may be deposited from either precursor moieties or from the material of the layer, as known in the art for forming such materials.

5 In one embodiment, the single ion conducting layer is deposited by a method selected from the group consisting of sputtering, electron beam evaporation, vacuum thermal evaporation, laser ablation, chemical vapor deposition, thermal evaporation, plasma enhanced chemical vacuum deposition, laser enhanced chemical vapor deposition, and jet vapor deposition.

10 In one embodiment, the polymer layer is deposited by a method selected from the group consisting of electron beam evaporation, vacuum thermal evaporation, laser ablation, chemical vapor deposition, thermal evaporation, plasma assisted chemical vacuum deposition, laser enhanced chemical vapor deposition, jet vapor deposition, and extrusion. The polymer layer may also be deposited by spin-coating methods.

15 A preferred method for deposition of crosslinked polymer layers is a flash evaporation method, for example, as described in U.S. Pat. No. 4,954,371 to Yializis. A preferred method for deposition of crosslinked polymer layers comprising lithium salts is a flash evaporation method, for example, as described in U.S. Pat. No 5,681,615 to Affinito *et al.*

20 Electrochemical Cells

The present invention provides an electrochemical cell comprising:

- (a) a cathode comprising a cathode active material;
 - (b) an anode; and
 - (c) a non-aqueous electrolyte interposed between the anode and the cathode,
- 25 wherein the anode comprises:
- (i) a first anode active layer comprising lithium metal, as described herein; and
 - (ii) a multi-layer structure, as described herein, in contact with a surface layer of the first layer; wherein the multi-layer structure comprises three or more
- 30 layers wherein each of the three or more layers comprises a layer selected from the group consisting of single ion conducting layers and polymer layers.

In a preferred embodiment, the cathode comprises an electroactive sulfur-containing material.

The present invention provides an electrochemical cell comprising:

(a) a cathode comprising a cathode active material;

5 (b) an anode; and

(c) a non-aqueous electrolyte interposed between the cathode and the anode.

wherein said anode comprises an anode active layer, which anode active layer comprises:

(i) a first layer comprising lithium metal

10 (ii) a second layer of a temporary protective material in contact with a surface of said first layer; and

(iii) a multi-layer structure in contact with a surface of the second layer;

wherein said temporary protective metal is capable of forming an alloy with lithium metal or is capable of diffusing into lithium metal.

15 In one embodiment, the metal of the temporary protective layer is selected from the group copper, magnesium, aluminum, silver, gold, lead, cadmium, bismuth, indium, gallium, germanium, zinc, tin, and platinum.

The temporary protective metal layer of the anode active layer may alloy with, diffuse with, dissolve into, blend with, or diffuse into with the lithium metal of the first layer prior to the electrochemical cycling cell or during the electrochemical cycling of a
20 cell

Suitable cathode active materials for use in the cathode of the electrochemical cells of the present invention include, but are not limited to, electroactive transition metal chalcogenides, electroactive conductive polymers, and electroactive sulfur-containing materials, and combinations thereof. As used herein, the term "chalcogenides" pertains to
25 compounds that contain one or more of the elements of oxygen, sulfur, and selenium. Examples of suitable transition metal chalcogenides include, but are not limited to, the electroactive oxides, sulfides, and selenides of transition metals selected from the group consisting of Mn, V, Cr, Ti, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, and Ir. In one embodiment, the transition metal chalcogenide is selected from the
30 group consisting of the electroactive oxides of nickel, manganese, cobalt, and vanadium, and the electroactive sulfides of iron. In one embodiment, the cathode active layer comprises an electroactive conductive polymer. Examples of suitable electroactive conductive polymers include, but are not limited to, electroactive and electronically

conductive polymers selected from the group consisting of polypyrroles, polyanilines, polyphenylenes, polythiophenes, and polyacetylenes. Preferred conductive polymers are polypyrroles, polyanilines, and polyacetylenes.

5 The term "electroactive sulfur-containing material," as used herein, relates to cathode active materials which comprise the element sulfur in any form, wherein the electrochemical activity involves the breaking or forming of sulfur-sulfur covalent bonds. Suitable electroactive sulfur-containing materials, include, but are not limited to, elemental sulfur and organic materials comprising sulfur atoms and carbon atoms, which may or may not be polymeric. Suitable organic materials include those further comprising
10 heteroatoms, conductive polymer segments, composites, and conductive polymers.

In one embodiment, the sulfur-containing material, in its oxidized form, comprises a polysulfide moiety, S_m , selected from the group consisting of covalent $-S_m-$ moieties, ionic $-S_m^-$ moieties, and ionic S_m^{2-} moieties, wherein m is an integer equal to or greater than 3. In one embodiment, m of the polysulfide moiety, S_m , of the sulfur-containing
15 polymer is an integer equal to or greater than 6. In one embodiment, m of the polysulfide moiety, S_m , of the sulfur-containing polymer is an integer equal to or greater than 8. In one embodiment, the sulfur-containing material is a sulfur-containing polymer. In one embodiment, the sulfur-containing polymer has a polymer backbone chain and the polysulfide moiety, S_m , is covalently bonded by one or both of its terminal sulfur atoms as
20 a side group to the polymer backbone chain. In one embodiment, the sulfur-containing polymer has a polymer backbone chain and the polysulfide moiety, S_m , is incorporated into the polymer backbone chain by covalent bonding of the terminal sulfur atoms of the polysulfide moiety.

In one embodiment, the electroactive sulfur-containing material comprises greater
25 than 50% by weight of sulfur. In a preferred embodiment, the electroactive sulfur-containing material comprises greater than 75% by weight of sulfur. In a more preferred embodiment, the electroactive sulfur-containing material comprises greater than 90% by weight of sulfur.

The nature of the electroactive sulfur-containing materials useful in the practice of
30 this invention may vary widely, as known in the art.

In one embodiment, the electroactive sulfur-containing material comprises elemental sulfur. In one embodiment, the electroactive sulfur-containing material comprises a mixture of elemental sulfur and a sulfur-containing polymer.

Examples of sulfur-containing polymers include those described in: U.S. Patent Nos. 5,601,947 and 5,690,702 to Skotheim *et al.*; U.S. Pat. Nos. 5,529,860 and 6,117,590 to Skotheim *et al.*; and U.S. Pat. Application Ser. No. 08/995,122 to Gorkovenko *et al.* of the common assignee and PCT Publication No. WO 99/33130. Other suitable
5 electroactive sulfur-containing materials comprising polysulfide linkages are described in U.S. Pat. No. 5,441,831 to Skotheim *et al.*; U.S. Pat. No. 4,664,991 to Perichaud *et al.*, and in U.S. Pat. Nos. 5,723,230, 5,783,330, 5,792,575 and 5,882,819 to Naoi *et al.* Still further examples of electroactive sulfur-containing materials include those comprising disulfide groups as described, for example in, U.S. Pat. No. 4,739,018 to Armand *et al.*; U.S. Pat.
10 Nos. 4,833,048 and 4,917,974, both to De Jonghe *et al.*; U.S. Pat. Nos. 5,162,175 and 5,516,598, both to Visco *et al.*; and U.S. Pat. No. 5,324,599 to Oyama *et al.*

The cathodes of the cells of the present invention may further comprise one or more conductive fillers to provide enhanced electronic conductivity. Examples of conductive fillers include, but are not limited to, those selected from the group consisting
15 of conductive carbons, graphites, activated carbon fibers, non-activated carbon nanofibers, metal flakes, metal powders, metal fibers, carbon fabrics, metal mesh, and electrically conductive polymers. The amount of conductive filler, if present, is preferably in the range of 2 to 30 % by weight of the cathode active layer. The cathodes may also further comprise other additives including, but not limited to, metal oxides, aluminas, silicas, and
20 transition metal chalcogenides.

The cathodes of the cells of the present invention may also comprise a binder. The choice of binder material may vary widely so long as it is inert with respect to the other materials in the cathode. Useful binders are those materials, usually polymeric, that allow for ease of processing of battery electrode composites and are generally known to those
25 skilled in the art of electrode fabrication. Examples of useful binders include, but are not limited to, those selected from the group consisting of polytetrafluoroethylenes (Teflon®), polyvinylidene fluorides (PVF₂ or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, and heat curable divinyl ethers, and the like. The amount of binder, if present, is preferably in the
30 range of 2 to 30% by weight of the cathode active layer.

The cathodes of the cells of the present invention may further comprise a current collector as is known in the art. Current collectors are useful in efficiently collecting the electrical current generated throughout the cathode and in providing an efficient surface for

attachment of the electrical contacts leading to the external circuit as well as functioning as a support for the cathode. Examples of useful current collectors include, but are not limited to, those selected from the group consisting of metallized plastic films, metal foils, metal grids, expanded metal grids, metal mesh, metal wool, woven carbon fabric, woven carbon mesh, non-woven carbon mesh, and carbon felt.

Cathodes of the cells of the present invention may be prepared by methods known in the art. For example, one suitable method comprises the steps of: (a) dispersing or suspending in a liquid medium the electroactive sulfur-containing material, as described herein; (b) optionally adding to the mixture of step (a) a conductive filler, binder, or other cathode additives; (c) mixing the composition resulting from step (b) to disperse the electroactive sulfur-containing material; (d) casting the composition resulting from step (c) onto a suitable substrate; and (e) removing some or all of the liquid from the composition resulting from step (d) to provide the cathode.

Examples of suitable liquid media for the preparation of the cathodes of the present invention include aqueous liquids, non-aqueous liquids, and mixtures thereof. Especially preferred liquids are non-aqueous liquids such as, for example, methanol, ethanol, isopropanol, propanol, butanol, tetrahydrofuran, dimethoxyethane, acetone, toluene, xylene, acetonitrile, and cyclohexane.

Mixing of the various components can be accomplished using any of a variety of methods known in the art, so long as the desired dissolution or dispersion of the components is obtained. Suitable methods of mixing include, but are not limited to, mechanical agitation, grinding, ultrasonication, ball milling, sand milling, and impingement milling.

The formulated dispersions can be applied to substrates by any of a variety of coating methods known in the art and then dried using techniques, known in the art, to form the solid cathodes of the lithium cells of this invention. Suitable hand coating techniques include, but are not limited to, the use of a wire-wound coating rod or gap coating bar. Suitable machine coating methods include, but are not limited to, the use of roller coating, gravure coating, slot extrusion coating, curtain coating, and bead coating. Removal of some or all of the liquid from the mixture can be accomplished by any of a variety of means known in the art. Examples of suitable methods for the removal of liquid from the mixture include, but are not limited to, hot air convection, heat, infrared radiation, flowing gases, vacuum, reduced pressure, and by simply air drying.

The method of preparing the cathodes of the present invention may further comprise heating the electroactive sulfur-containing material to a temperature above its melting point and then resolidifying the melted electroactive sulfur-containing material to form a cathode active layer having a reduced thickness and a redistributed sulfur-containing material of higher volumetric density than before the melting process.

The electrolytes used in electrochemical or battery cells function as a medium for the storage and transport of ions, and in the special case of solid electrolytes and gel electrolytes, these materials may additionally function as a separator between the anode and the cathode. Any liquid, solid, or gel material capable of storing and transporting ions may be used, so long as the material is electrochemically and chemically unreactive with respect to the anode and the cathode, and the material facilitates the transport of lithium ions between the anode and the cathode. The electrolyte must also be electronically non-conductive to prevent short circuiting between the anode and the cathode.

Typically, the electrolyte comprises one or more ionic electrolyte salts to provide ionic conductivity and one or more non-aqueous liquid electrolyte solvents, gel polymer materials, or polymer materials. Suitable non-aqueous electrolytes for use in the present invention include, but are not limited to, organic electrolytes comprising one or more materials selected from the group consisting of liquid electrolytes, gel polymer electrolytes, and solid polymer electrolytes. Examples of non-aqueous electrolytes for lithium batteries are described by Dominey in *Lithium Batteries, New Materials, Developments and Perspectives*, Chapter 4, pp. 137-165, Elsevier, Amsterdam (1994). Examples of gel polymer electrolytes and solid polymer electrolytes are described by Alamgir *et al.* in *Lithium Batteries, New Materials, Developments and Perspectives*, Chapter 3, pp. 93-136, Elsevier, Amsterdam (1994).

Examples of useful non-aqueous liquid electrolyte solvents include, but are not limited to, non-aqueous organic solvents, such as, for example, N-methyl acetamide, acetonitrile, acetals, ketals, esters, carbonates, sulfones, sulfites, sulfolanes, aliphatic ethers, cyclic ethers, glymes, polyethers, phosphate esters, siloxanes, dioxolanes, N-alkylpyrrolidones, substituted forms of the foregoing, and blends thereof. Fluorinated derivatives of the foregoing are also useful as liquid electrolyte solvents.

Liquid electrolyte solvents are also useful as plasticizers for gel polymer electrolytes. Examples of useful gel polymer electrolytes include, but are not limited to, those comprising one or more polymers selected from the group consisting of polyethylene

oxides, polypropylene oxides, polyacrylonitriles, polysiloxanes, polyimides, polyphosphazenes, polyethers, sulfonated polyimides, perfluorinated membranes (NAFIONTM resins), polydivinyl polyethylene glycols, polyethylene glycol diacrylates, polyethylene glycol dimethacrylates, derivatives of the foregoing, copolymers of the
5 foregoing, crosslinked and network structures of the foregoing, and blends of the foregoing, and optionally, one or more plasticizers.

Examples of useful solid polymer electrolytes include, but are not limited to, those comprising one or more polymers selected from the group consisting of polyethers, polyethylene oxides, polypropylene oxides, polyimides, polyphosphazenes,
10 polyacrylonitriles, polysiloxanes, derivatives of the foregoing, copolymers of the foregoing, crosslinked and network structures of the foregoing, and blends of the foregoing.

In addition to electrolyte solvents, gelling agents, and polymers as known in the art for forming non-aqueous electrolytes, the non-aqueous electrolyte may further comprise
15 one or more ionic electrolyte salts, also as known in the art, to increase the ionic conductivity.

Examples of ionic electrolyte salts for use in the electrolytes of the present invention include, but are not limited to, LiSCN, LiBr, LiI, LiClO₄, LiAsF₆, LiSO₃CF₃, LiSO₃CH₃, LiBF₄, LiB(Ph)₄, LiPF₆, LiC(SO₂CF₃)₃, and LiN(SO₂CF₃)₂. Other electrolyte
20 salts useful in the practice of this invention include lithium polysulfides (Li₂S_x), and lithium salts of organic ionic polysulfides (LiS_xR)_n, where x is an integer from 1 to 20, n is an integer from 1 to 3, and R is an organic group, and those disclosed in U.S. Pat. No. 5,538,812 to Lee *et al.* Preferred ionic electrolyte salts are LiBr, LiI, LiSCN, LiBF₄, LiPF₆, LiAsF₆, LiSO₃CF₃, LiN(SO₂CF₃)₂, and LiC(SO₂CF₃)₃.

25 The electrochemical cells of the present invention may further comprise a separator interposed between the cathode and anode. Typically, the separator is a solid non-conductive or insulative material which separates or insulates the anode and the cathode from each other preventing short circuiting, and which permits the transport of ions between the anode and the cathode.

30 The pores of the separator may be partially or substantially filled with electrolyte. Separators may be supplied as porous free standing films which are interleaved with the anodes and the cathodes during the fabrication of cells. Alternatively, the porous separator layer may be applied directly to the surface of one of the electrodes, for example, as

described in PCT Publication No. WO 99/33125 to Carlson *et al.* and in U.S. Pat. No. 5,194,341 to Bagley *et al.*

5 A variety of separator materials are known in the art. Examples of suitable solid porous separator materials include, but are not limited to, polyolefins, such as, for example, polyethylenes and polypropylenes, glass fiber filter papers, and ceramic materials. Further examples of separators and separator materials suitable for use in this invention are those comprising a microporous xerogel layer, for example, a microporous pseudo-boehmite layer, which may be provided either as a free standing film or by a direct coating application on one of the electrodes, as described in U.S. Pat. Application Ser.
10 Nos. 08/995,089 and 09/215,112 by Carlson *et al.* of the common assignee. Solid electrolytes and gel electrolytes may also function as a separator in addition to their electrolyte function.

In one embodiment, the solid porous separator is a porous polyolefin separator. In one embodiment, the solid porous separator comprises a microporous xerogel layer. In
15 one embodiment, the solid porous separator comprises a microporous pseudo-boehmite layer.

Battery cells of the present invention may be made in a variety of sizes and configurations as known to those skilled in the art. These battery design configurations include, but are not limited to, planar, prismatic, jelly roll, w-fold, stacked, and the like.

20 The electrochemical cells comprising the anodes of the present invention may be either primary or secondary batteries or cells.

Another aspect of the present invention pertains to a method of forming an electrochemical cell, the method comprising the steps of: (i) providing a cathode; (ii) providing an anode, as described herein; and, (iii) interposing an electrolyte between the
25 anode and the cathode.

While the invention has been described in detail and with reference to specific and general embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS

1. An electrochemical cell comprising:
 - 5 (a) a cathode comprising an electroactive sulfur-containing material;
 - (b) an anode; and
 - (c) a non-aqueous electrolyte interposed between said anode and said cathode, wherein said anode comprises:
 - (i) a first anode active layer comprising lithium metal; and
 - 10 (ii) a multi-layer structure in contact with a surface layer of said first anode active layer, wherein said multi-layer structure comprises three or more layers, wherein each of said three or more layers comprises a layer selected from the group consisting of single ion conducting layers and polymer layers.
- 15 2. The cell of claim 1, wherein the thickness of said first anode active layer is 2 to 100 microns.
3. The cell of claim 1, wherein the thickness of said multi-layer structure is 0.5 to 10 microns.
- 20 4. The cell of claim 1, wherein the thickness of said multi-layer structure is 1 to 5 microns.
5. The cell of claim 1, wherein said multi-layer structure comprises four or more layers.
- 25 6. The cell of claim 1, wherein said multi-layer structure further comprises a metal alloy layer, wherein said metal alloy comprises a metal selected from the group consisting of Zn, Mg, Sn, and Al.

7. The cell of claim 1, wherein said single ion conducting layer of said multi-layer structure comprises a glass selected from the group consisting of lithium silicates, lithium borates, lithium aluminates, lithium phosphates, lithium phosphorus oxynitrides, lithium silicosulfides, lithium germanosulfides, lithium lanthanum oxides, lithium tantalum oxides, lithium niobium oxides, lithium titanium oxides, lithium borosulfides, lithium aluminosulfides, and lithium phosphosulfides, and combinations thereof.
8. The cell of claim 7, wherein said single ion conducting layer of said multi-layer structure is a lithium phosphorus oxynitride.
9. The cell of claim 1, wherein said polymer layer of said multi-layer structure comprises a polymer layer formed from the polymerization of one or more acrylate monomers selected from the group consisting of alkyl acrylates, glycol acrylates, and polyglycol acrylates.
10. The cell of claim 1, wherein said non-aqueous electrolyte is a liquid electrolyte.
11. The cell of claim 1, wherein said first anode active layer further comprises an intermediate layer selected from the group consisting of temporary protective metal layers and plasma CO₂ treatment layers, wherein said intermediate layer is interposed between said first anode active layer and said multi-layered structure.
12. The cell of claim 1, wherein said anode further comprises a substrate, wherein said substrate is in contact with a surface of said first anode active layer on the side opposite to said multi-layered structure.
13. The cell of claim 12, wherein said substrate is selected from the group consisting of metal foils, polymer films, metallized polymer films, electrically conductive polymer films, polymer films having an electrically conductive coating, electrically conductive polymer films having an electrically conductive metal coating, and polymer films having conductive particles dispersed therein.

14. The cell of claim 1, wherein said electroactive sulfur-containing material comprises elemental sulfur.
- 5 15. An anode of an electrochemical cell, wherein said anode comprises:
- (i) a first anode active layer comprising lithium metal; and
 - (ii) a multi-layer structure in contact with a surface of said first anode active layer;
- 10 wherein said multi-layer structure comprises three or more layers, and wherein each of said three or more layers comprises a layer selected from the group consisting of ion conducting layers and polymer layers.
16. The anode of claim 15, wherein said multi-layer structure comprises four or more layers.

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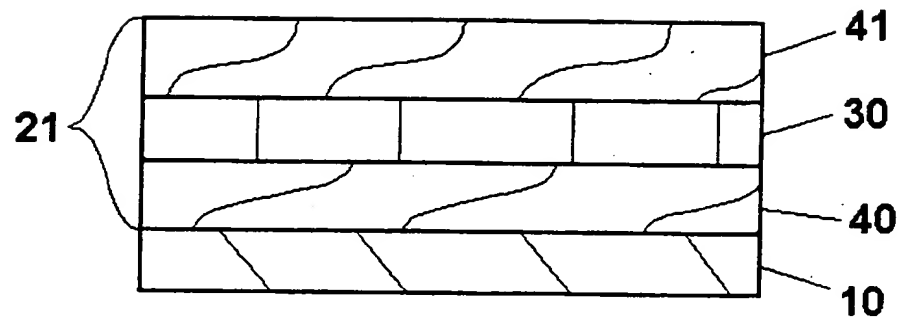


Figure 1

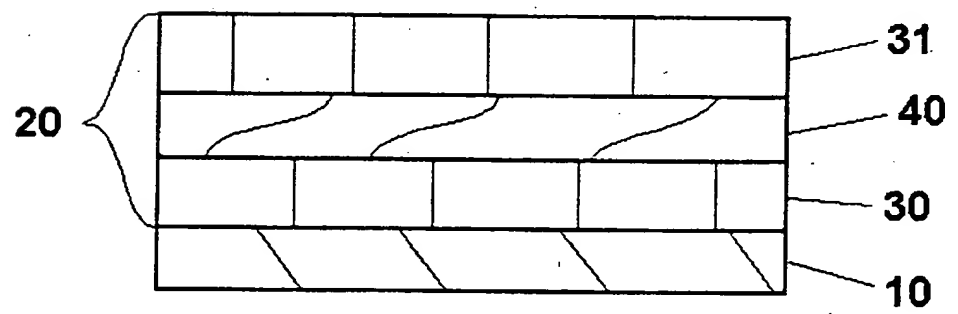


Figure 2

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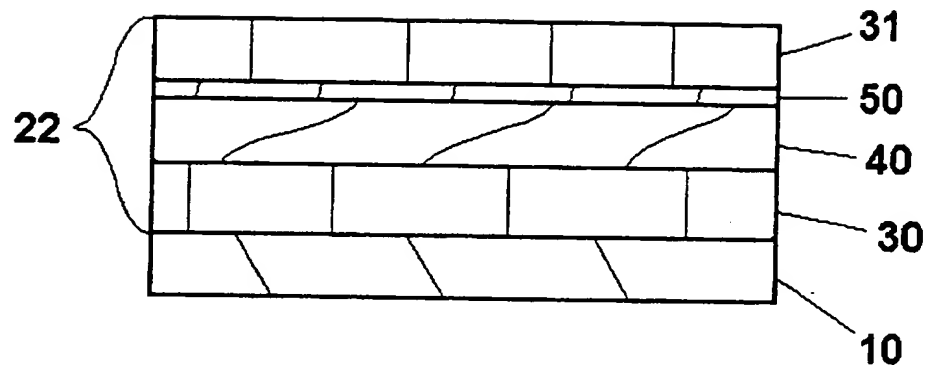


Figure 3

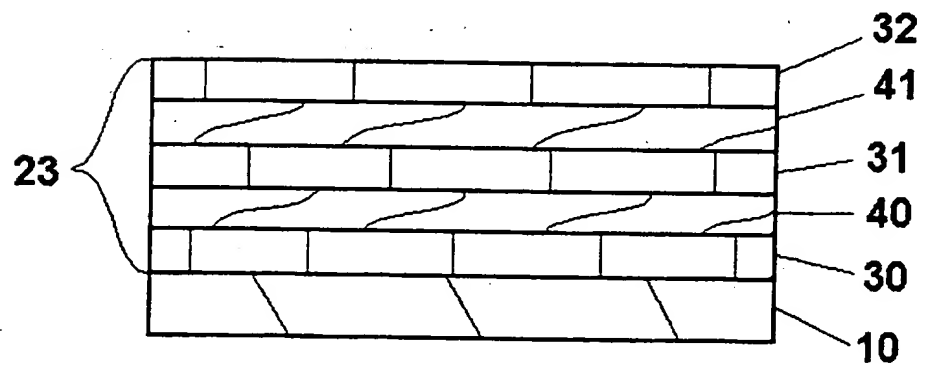


Figure 4

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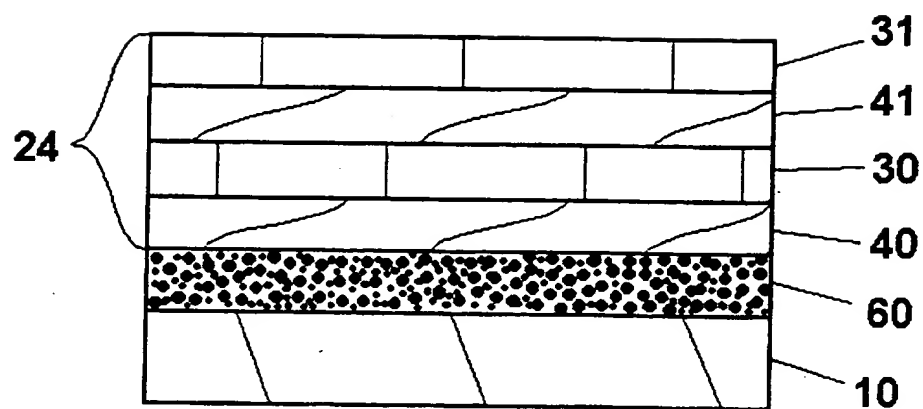


Figure 5

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/32232

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M4/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A A	<p>US 5 462 566 A (SKOTHEIM TERJE A) 31 October 1995 (1995-10-31) column 3, line 25 - line 39 column 4, line 27 - line 57 column 5, line 10 - line 45 claims 1-3</p> <p>US 5 648 187 A (SKOTHEIM TERJE ABSJORN) 15 July 1997 (1997-07-15) column 2, line 35 - line 46 column 3, line 25 - line 27 column 5, line 23 - line 38 claims 1,11,17,26</p> <p style="text-align: center;">-/-</p>	<p>1,5,15, 16 2-4,6-14</p> <p>1,3-5,9, 14,15</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

9 February 2001

Date of mailing of the international search report

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Métais, S

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 00/32232

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 415 954 A (BELANGER ANDRE ET AL) 16 May 1995 (1995-05-16) column 1, line 21 - line 47 column 6, line 32 - line 44 column 8, line 12 - line 51 claims 7,16,19,25,32</p>	1,6,11
A	<p>US 5 366 829 A (SAIDI EILEEN S) 22 November 1994 (1994-11-22) column 3, line 17 - line 66 column 6, line 55 - line 60 column 7, line 46 - line 54 claims 1,3</p>	1,9,15

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Information on patent family members

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